J Polym Res (2012) 19:13
DOI 10.1007/s10965-012-0013-4

ORIGINAL PAPER

Effects of adding different ethanol amines during membrane preparation on the performance and morphology of nanoporous PES membranes

Y. Mansourpanah · A. Gheshlaghi

Received: 3 June 2012 / Accepted: 16 October 2012 / Published online: 6 November 2012

Abstract In this study, different ethanol amines (EAs) were added at various concentrations during the production of membranes. The effects of adding these EAs on the performance and morphology of membranes 200 μm and 280 μm thick were investigated. The membranes were obtained via a phase-inversion procedure using polyethersulfone as the base polymer, DMAc as the solvent, and polyvinylpyrrolidone as a pore former. The flux behavior and rejection abilities of these membranes were studied using a crossflow setup. The effects of adding the different ethanol amines during the preparation of membranes on the flux and rejection of these membranes varied significantly. The results showed that membrane performance in the presence of these additives is strongly related to the thickness of the casting film as well as the type of ethanol amine added. Cross-sectional SEM images indicated that these additives have striking effects on the membrane morphology. Diethanol amine is able to increase the fraction of Na_2SO_4 rejected by the membrane from 70 to near 90 %. The data obtained in this work illustrate that among all of the EAs tested, diethanol amine exerts the greatest effect on membrane performance.

Keywords Membrane preparation · Phase inversion · Ethanol amines · Morphological study

Y. Mansourpanah (✉)
Department of Applied Chemistry, Lorestan University,
Khorramabad, Iran
e-mail: jmansourpanah@yahoo.com

Y. Mansourpanah
e-mail: mansourpanah.y@lu.ac.ir

A. Gheshlaghi
East Tehran Branch, Department of Applied Chemistry,
Islamic Azad University,
Tehran, Iran

Introduction

Polymeric membranes are used for a variety of industrial applications, such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis, and gas separation [1]. The high-T_g polymer polyethersulfone (PES), which exhibits high mechanical, thermal, and chemical resistance, is widely used in the manufacture of asymmetric membranes [2, 3]. PES shows favorable temperature resistance, tolerates a wide range of pH values, and exhibits good resistance to chlorine and other chemicals [4].

There are several ways to fabricate polymeric membranes, such as track etching, sintering, stretching, and phase separation. The morphology of the resulting membrane strongly depends on the properties of the materials used to fabricate it and the process conditions employed. One well-known procedure for fabricating membranes is immersion precipitation [5–7]. In this process, an asymmetric structure comprising a dense top layer and a porous sublayer is created. Adding tiny amounts of organic/inorganic additives to the dope solution produces significant effects on membrane morphology and performance [8–10]. Polyethyleneglycol (PEG) and polyvinylpyrrolidone (PVP) are widely used in casting solutions to change the morphology and performance of the membrane produced [11–13]. Adding these additives leads to low membrane fouling, high flux, selectivity, and other advantages [14–17].

In the work described in the present paper, for the first time, the effects on membrane performance and morphology of adding different ethanol amines (EAs) during the preparation of those membranes were investigated. Ethanol amine, diethanol amine, and triethanol amine with different functional groups (–OH and –NH) were added to the casting solution, and the morphologies and performances of the resulting membranes were studied. Upon performing a comprehensive study of the relevant literature in this field, we did not find any report of research similar to that described

here. The structures of the different EAs added to the casting solution are depicted in Scheme 1. SEM analysis was used to elucidate how varying the EA added affects the morphology and structure of the resulting membrane. The flux and rejection properties of the membranes were studied using a crossflow setup.

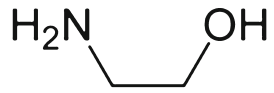
Experimental

Materials and apparatus

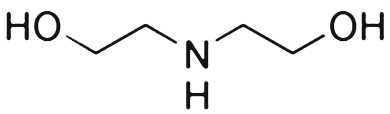
Polyethersulfone (PES Ultrason E6020P with M_W=50,000 g/mol) was supplied by BASF (Ludwigshafen, Germany). Polyvinylpyrrolidone (PVP, 40,000 g/mol), ethanol amine, diethanol amine, triethanol amine, and acrylic acid were from Merck (Darmstadt, Germany). Dimethylacetamide (DMAc) was purchased from Scharlau (Sentmenat, Spain). Na_2SO_4 was used to investigate the ion rejection capabilities of the membranes. Distilled water was used throughout the study.

Membrane composition and preparation procedure

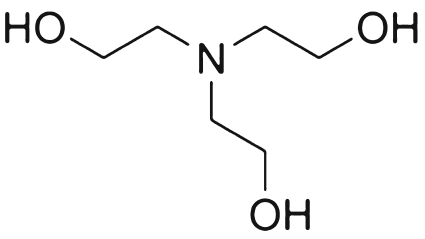
Casting solutions were prepared by mixing 18 wt% PES in dimethylacetamide (DMAc) with one of three ethanol amines (either ethanol amine, diethanol amine, or triethanol amine) at one of three different concentrations (either 3, 5, or 10 wt%), as well as 3 wt% polyvinylpyrrolidone (PVP) used as the pore former. Stirring was performed at 200 rpm for 5 h at 40 °C. After a homogeneous solution had been generated, the dope solution was held at ambient temperature for around 24 h to remove air bubbles. Afterwards, the dope solution was cast onto a glass support at a thickness of either 200 μm or 280 μm using a film applicator at room temperature without evaporation. After coating, the casting film was immersed into a distilled water bath for at least 20 h to remove most of the solvent and water-soluble additives.



Ethanol amine (61 g/mol)



Diethanol amine (105.1 g/mol)



Triethanol amine (149.2 g/mol)

Scheme 1 Molecular structures of the different ethanol amines added to the membrane casting solution

SEM characterization

The cross-section of each membrane was examined using a scanning electron microscope (SEM). The samples of the membranes were frozen in liquid nitrogen and fractured. After sputtering with gold, they were viewed with a Philips (Eindhoven, The Netherlands) SEM at 25 kV.

Membrane performance evaluation

The performance of each membrane was analyzed using a crossflow system. The details of the experimental setup used have been provided elsewhere [18]. The membrane surface area in the filtration cell was 22 cm^2. The membrane flux was determined at 10 min intervals under a transmembrane pressure of 1.0 MPa. The experiments were carried out at 25 °C. The crossflow velocity was approximately 0.6 m/s in all tests. The permeation rate and salt rejection were determined for each membrane using Na_2SO_4 solution at a concentration of 1000 ppm. The membrane rejection was obtained using

$$R\% = \left[1 - \frac{\lambda_p}{\lambda_f}\right] \times 100, \quad (1)$$

where λ_p and λ_f are the ion conductivity in the permeate and feed, respectively. The ion rejection of the membrane was investigated by measuring the permeate conductivity using a conductivity meter (model 8733, Hanna Instruments, Woonsocket, RI, USA).

Results and discussion

Membranes with a thickness of 200 μm

The effects of adding different concentrations of ethanol amine during membrane preparation on the characteristics of a membrane 200 μm thick are shown in Figs. 1 and 2. According to these figures, adding the ethanol amine clearly alters membrane morphology and performance. Cross-sectional SEM images of membranes 200 μm thick prepared in the presence of various concentrations of ethanol amine

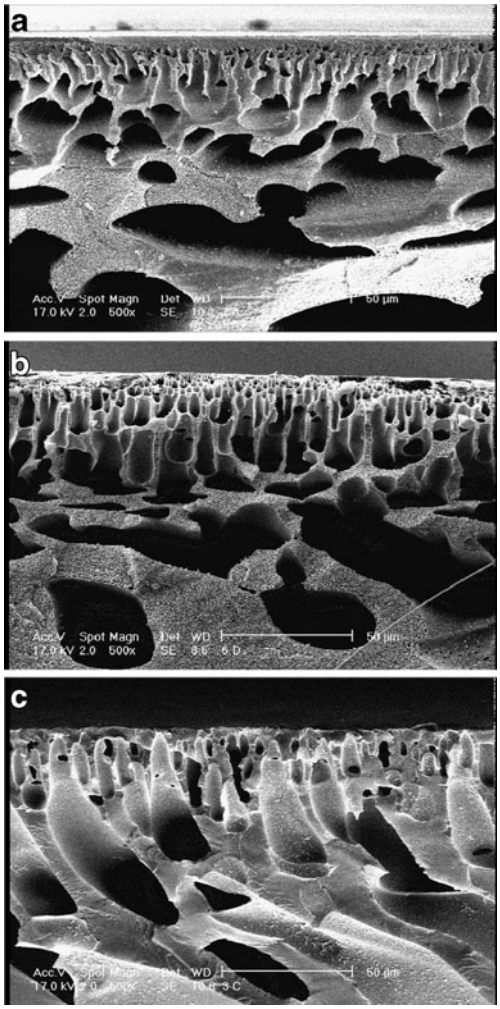


Fig. 1a–c Cross-sectional SEM images of membranes (200 μm thickness) prepared in the presence of **a** 0 wt% **b** 3 wt%, and **c** 10 wt% of ethanol amine

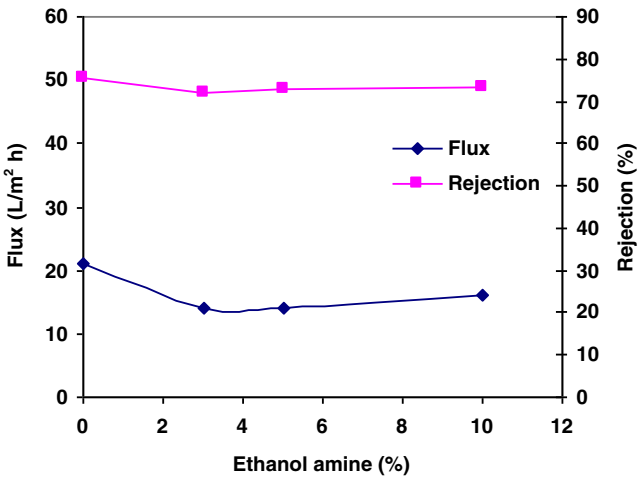


Fig. 2 Effects of adding different concentrations of ethanol amine during membrane preparation on the flux and rejection of membranes with 200 μm thickness

are shown in Fig. 1. As seen in this figure, adding ethanol amine changes the structure of the membrane obtained. The neat PES membrane possesses a structure with big macrovoids. The membrane prepared in the presence of 3 wt% ethanol amine also shows macrovoids, although they are slightly smaller than those seen in the neat PES membrane. Figure 2 illustrates the effects of adding different concentrations of ethanol amine during membrane preparation on membrane flux and rejection. Based on this figure, the flux decreases from 21 to near 14 L/m^{2}h as the concentration of ethanol amine is increased. The presence of big macrovoids in the neat PES membrane allows a higher flux. On the other hand, the rejection parameter for all of the membranes was ~74 %, whatever the concentration of ethanol amine. Upon increasing the additive concentration to 10 wt%, a membrane with a thin skin layer and finger-like pores was formed (Fig. 1c), resulting in a slight increase in flux. The formation of finger-like pores causes a reduction in flux but the thinner skin layer (compared to neat PES; see Fig. 1) causes more flux. Therefore, we have two opposite effects, leading to no significant change in membrane performance. Figure 1a (for 0 wt% additive) clearly shows a few big pores in the membrane structure. In Fig. 1c (for 10 wt% additive), big macrovoids in the membrane structure are hidden and have changed to finger-like pores.

Immersing the cast film into a distilled water bath initiates precipitation. Solvent/nonsolvent exchange takes place and nuclei of the polymer-poor phase form. These nuclei continue to grow until the polymer concentration at the pore/solution interface becomes high enough for solidification to occur. Under instantaneous demixing conditions, the composition of the nuclei remains stable for a long period. Generally, macrovoids are formed where instantaneous demixing takes place [19]. The conversion of big macrovoids to finger-like pores reduces flux. Increasing the amount of ethanol amine probably changes the diffusion rates of the solvent and nonsolvent, leading to delayed demixing. The occurrence of delayed or instantaneous demixing is influenced by thermodynamic stability and kinetic processes. When an additive is added to the casting solution, its thermodynamic stability is changed. On the other hand, the addition of additives to the casting solution can affect the solvent/nonsolvent exchange rate, resulting in kinetic effects [13, 14]. According to the literature, additives with different structures exert different effects on the properties of the membrane. These effects are due to the attraction of the additive to the polymer chains and its affinity for the solvent or nonsolvent. These effects are important for EAs with –OH or –NH functional groups. For instance, the presence of these hydrophilic functional groups in the casting solution increases the affinity and the exchange rate of nonsolvent for diffusion through the membrane bulk.

Adding diethanol amine during membrane preparation leads to a sharp decrease in the rejection of the resulting membrane from 75 % to near 46 % (Fig. 3). This value indicates that the flux reaches about 55 L/m^{2}h when 5 wt% diethanol amine is added but decreases to 47 L/m^2 h when 10 wt% diethanol amine is added. Upon comparing the SEM images of membranes containing 3 wt% ethanol amine (Fig. 2b) and diethanol amine (Fig. 4), it is clear that adding the diethanol amine leads to much bigger and more open macrovoids in the membrane. In addition, the number and shape of the pores close to the surface differ depending on whether 3 wt% ethanol amine or diethanol amine is added. The number of pores increase and the shape of the pores change from a closed to a more open shape upon shifting the additive from 3 wt% ethanol amine to diethanol amine. This is probably because thermodynamic instability overcomes the kinetic process, leading to a more porous structure [20, 21].

Based on the discussion above, when 10 wt% diethanol amine is added, the increase in additive concentration causes a small increase in the solvent/nonsolvent exchange rate in the resulting membrane, which results in a slight decrease in flux.

Figure 5 shows the effect of adding triethanol amine during membrane preparation on membrane performance. The resulting membranes behave similarly to the membranes prepared in the presence of ethanol amine. The membrane rejection decreases from approximately 75 % to 71 % with increasing triethanol amine. Upon viewing the SEM image of the membrane with 3 wt% triethanol amine shown in Fig. 6, structural alterations are observable. Smaller macrovoids (closed, sponge-like pores) are apparent, and the number of pores close to the surface is slightly decreased compared to, say, the structure of a membrane with 3 wt% ethanol amine (see Fig. 4a). Generally, using additives increases the viscosity of the casting solution,

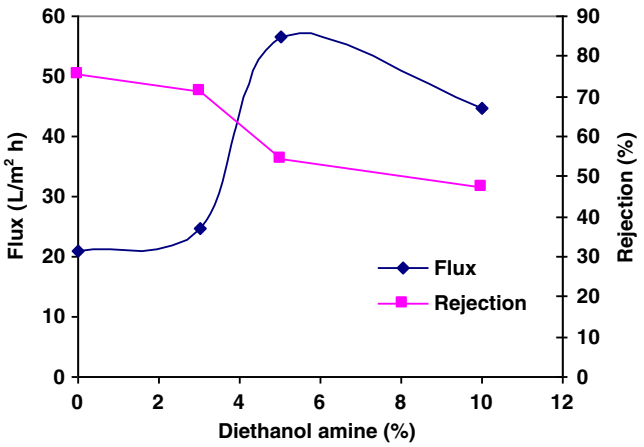


Fig. 3 Effects of adding different concentrations of diethanol amine during membrane preparation on membrane flux and rejection

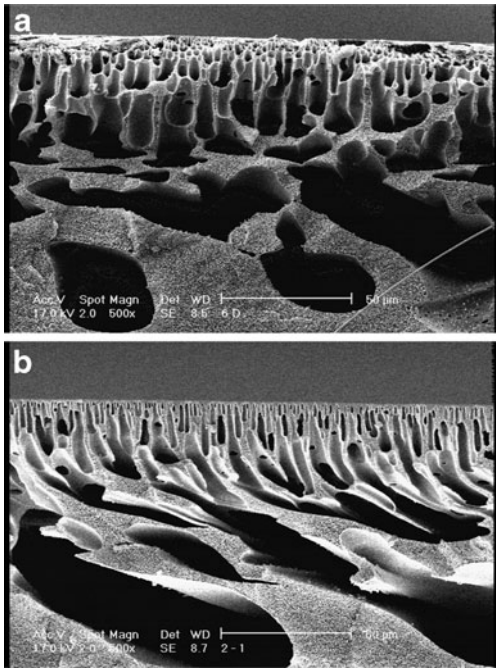


Fig. 4a–b SEM images of membranes including **a** 3 % ethanol amine and **b** 3 % diethanol amine

which has significant thermodynamic and kinetic effects. We believe that the presence of the triethanol amine has a marked effect on the kinetics, leading to lower solvent/nonsolvent exchange and a less porous structure. Thus, the membranes with triethanol amine show relatively low flux.

Membranes with a thickness of 280 μm

The performances of membranes 280 μm thick were also investigated. The results obtained show that adding different ethanol amines during the preparation of these thicker

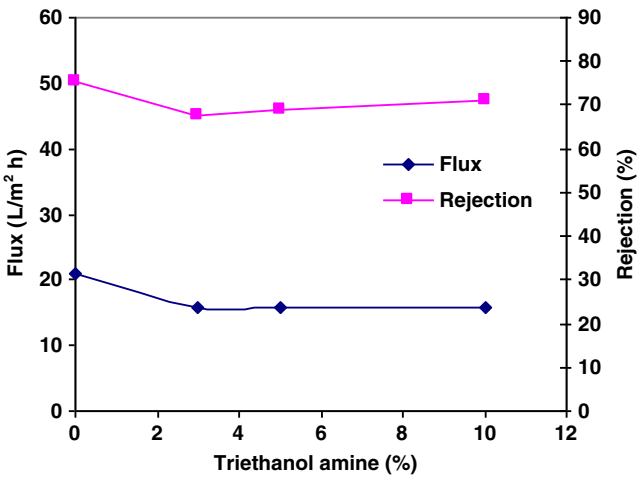


Fig. 5 Effects of adding different concentrations of triethanol amine during membrane preparation on the flux and rejection of membranes with 200 μm thickness

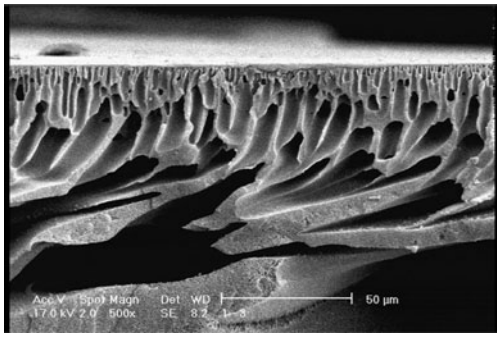


Fig. 6 SEM image of membrane that includes 3 % triethanol amine

membranes has quite different effects to those seen for the 200 µm thick membranes. According to Fig. 7, as the amount of ethanol amine added during membrane preparation increases, the flux of the resulting membrane initially decreases to 13 L/m^{2}h (for 3 wt% ethanol amine) and then rises to around 31 L/m^{2}h (for 10 wt% ethanol amine). For these thicker membranes, changes in membrane rejection are well correlated with flux changes. Rejection initially increases to 77 % (for 3 wt% ethanol amine) and then falls to around 61 % (for 10 wt% ethanol amine). Remarkable changes were observed when diethanol amine was added during the preparation of membranes 280 µm thick (Fig. 8). The rejection parameter increased to around 90 % for 10 wt% diethanol amine, while the flux decreased to 11 L/m^{2}h. On the other hand, when triethanol amine was added during membrane preparation, no significant changes in the ability of the resulting membrane to reject Na_2SO_4 were observed with increasing triethanol amine (Fig. 9), but the membrane flux decreased from 29 to 10 L/m^{2}h.

It is clear that different ethanol amines have different effects on the membrane morphology and performance, and these effects also depend on the casting film thickness. Figure 10 compares SEM images of membranes that are

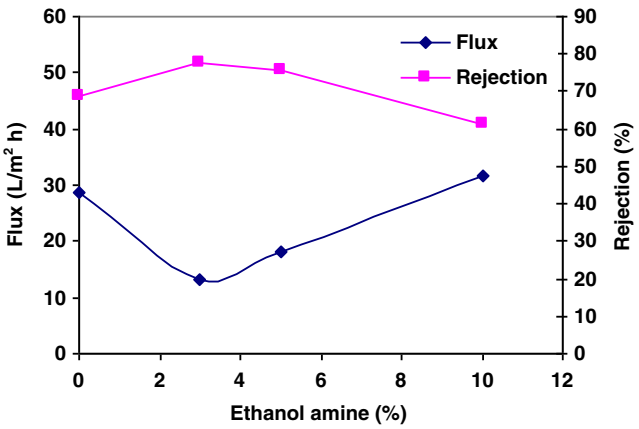


Fig. 7 Effects of adding different concentrations of ethanol amine during membrane preparation on the flux and rejection of membranes with 280 µm thickness

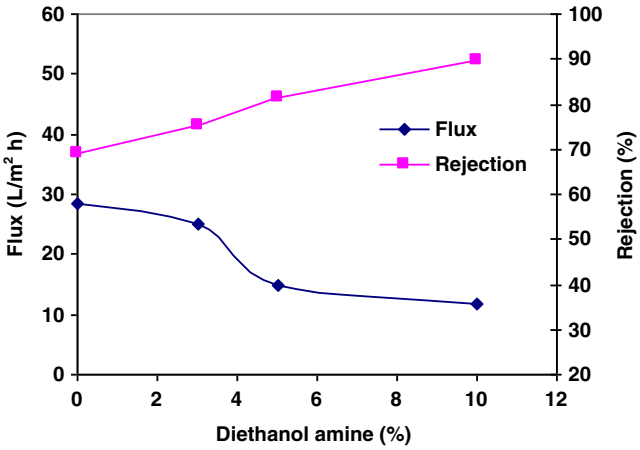


Fig. 8 Effects of adding different concentrations of diethanol amine during membrane preparation on the flux and rejection of membranes with 280 µm thickness

200 µm thick (Fig. 10a) and 280 µm thick (Fig. 10b), both of which contain 3 wt% ethanol amine. The rate of diffusional solvent/nonsolvent exchange probably decreases with increasing film thickness, which leads to delayed demixing, hindering the growth of the polymer-poor phase. This phenomenon leads to the formation of a membrane without big macrovoids. This, in turn, causes a lower flux and a higher rejection parameter. The flux of the 200 µm thick membranes containing triethanol amine decreased from about 21 to around 14 L/m^{2}h with increasing triethanol amine, whereas the flux of the 280 µm thick membranes containing triethanol amine decreased from about 29 to around 10 L/m^{2}h with increasing triethanol amine. Furthermore, thickening the membrane increases the rejection parameter due to enhanced resistance of the membrane to material transfer. If we consider the SEM images obtained for both membrane thicknesses, we can conclude that the kinetic process dominates over the thermodynamic instability for the thicker

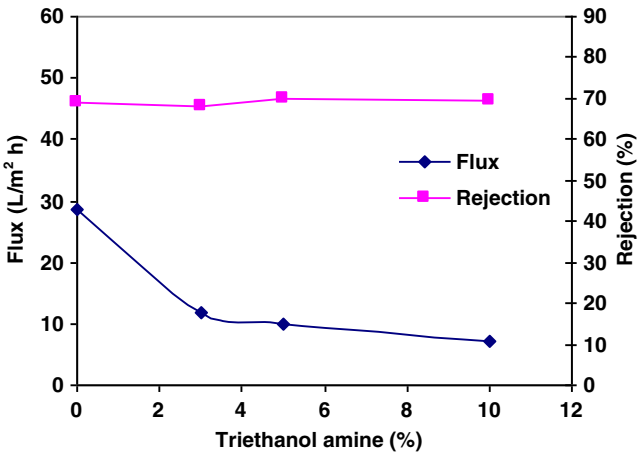


Fig. 9 Effects of adding different concentrations of triethanol amine during membrane preparation on the flux and rejection of membranes with 280 µm thickness

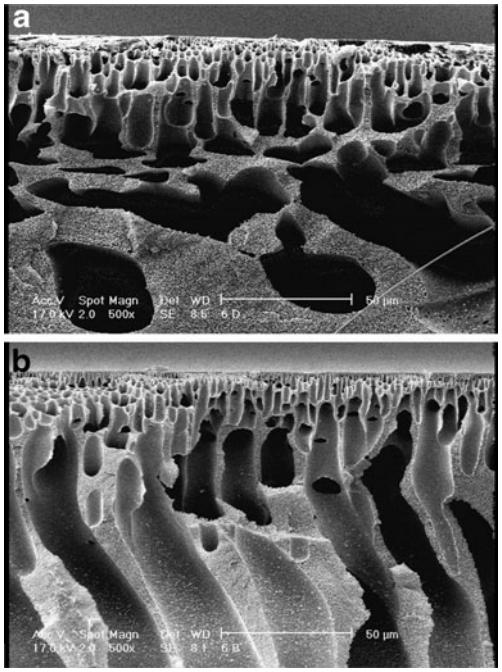


Fig. 10a–b Comparing the morphologies of two membranes that both include 3 wt% ethanol amine but are different thicknesses. Membrane thickness: **a** 200 μm; **b** 280 μm

membrane. Accordingly, we can see that the effects of additives on membrane performance and morphology strongly depend on membrane thickness. As can be seen in this study, the effects of adding ethanol amine during membrane preparation depend on not only the type of

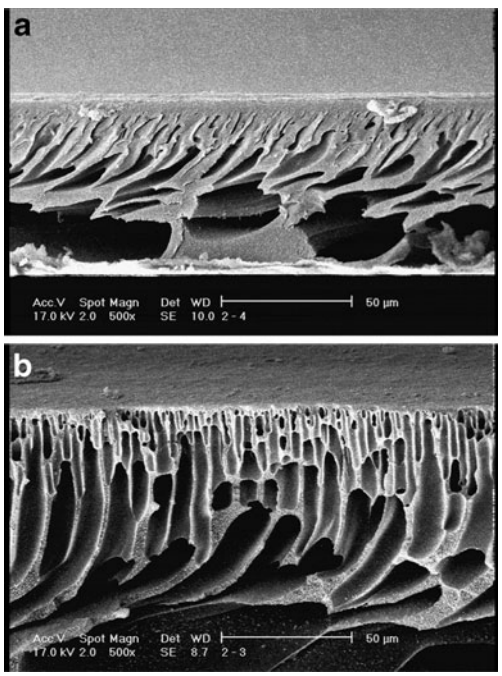


Fig. 11a–b SEM images of two membranes that both include 10 wt% triethanol amine but are different thicknesses. Membrane thickness: **a** 200 μm; **b** 280 μm

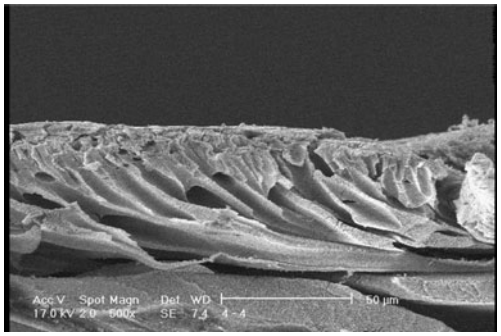


Fig. 12 SEM image of membrane that includes 3 wt% diethanol amine and is 280 μm thickness

ethanol amine added but also (strongly on) the thickness of the casting film. SEM images of two membranes with different thicknesses that both include 10 wt% triethanol amine (see Fig. 11) clearly prove the above statements. Figure 11a shows a 200 μm thick membrane containing a structure that includes large macrovoids. In contrast, the corresponding 280 μm thick membrane shows a more uniform structure without the big macrovoids.

Upon comparing SEM images of two membranes with different thicknesses that both contain 3 wt% diethanol amine, we can see a denser, macrovoid-free structure in the 280 μm thick membrane (see Fig. 12). When diethanol amine is added during the preparation of a 200 μm thick membrane, thermodynamic instability probably dominates over the kinetic process, resulting in a more porous membrane [22, 23].

Among the three ethanol amines added in this work, adding diethanol amine led to the best-performing membranes with suitable rejection parameters for Na_2SO_4. This is probably due to the properties of diethanol amine, specifically (i) its basicity and (ii) the number of –OH groups present. The basicity and the number of –OH groups decrease for the ethanol amines in the order: triethanol amine > diethanol amine > ethanol amine. Maybe increasing the basicity affects the interactions between polymer chains and reduces interchain attraction. A more open structure may then be formed. On the other hand, increasing the number of –OH groups can affect the miscibility of the solvent and nonsolvent, leading to delayed demixing. However, diethanol amine is a relatively weak base with two –OH functional groups, so it has only a moderate effect during membrane formation, causing a macrovoid-free membrane when the casting solution film is relatively thick.

Conclusions

This study clearly shows that the effects of additives on membrane performance and morphology depend strongly on the casting solution thickness as well as the type of additive

used. Different ethanol amines (ethanol amine, diethanol amine, and triethanol amine) used as additives were found to have different effects on the membrane morphology, and their effects also varied for casting solution films with different thicknesses. For thicker membranes, the kinetic process is dominant. On the other hand, thermodynamic instability overcomes the kinetic process when the casting solution film is relatively thin. Membrane rejection was optimal for a 280 μm thick membrane with diethanol amine as an additive.

References

1. Mulder M (1992) Basic principles of membrane technology. Kluwer, Dordrecht
2. Chaturvedi BK, Ghosh AK, Ramachandhran V, Trivedi MK, HanTa MS, Misra BM (2001) Preparation, characterization and performance of polyethersulfone ultrafiltration membranes. Desalination 133:31–40
3. Barth C, Gonçalves MC, Pires ATN, Roeder J, Wolf BA (2000) Asymmetric polysulfone and polyethersulfone membranes: effects of thermodynamic conditions during formation on their performance. J Membr Sci 169:287–299
4. Cheryan M (1998) Ultrafiltration and microfiltration handbook. Technomic, Lancaster
5. Liu Y, Koops GH, Sthratmann H (2003) Characterization of morphology controlled polyethersulfone hollow fiber membranes by addition of polyethylene glycol to the dope and bore liquid solution. J Membr Sci 223:187–199
6. Mansourpanah Y, Madaeni SS, Rahimpour A, Adeli M, Hashemi MY (2011) Fabrication new PES-based mixed matrix nanocomposite membranes using polycaprolactone modified carbon nanotubes as the additive: property changes and morphological studies. Desalination 277:171–177
7. Mansourpanah Y, Madaeni SS, Rahimpour A, Kheirollahi Z, Adeli M (2010) Changing the performance and morphology of polyethersulfone/polyimide blend nanofiltration membranes using trimethylamine. Desalination 256:101–107
8. Yeo HT, Lee ST, Han MJ (2000) Role of polymer additive in casting solution in preparation of phase inversion polysulfone membranes. J Chem Eng Japan 33:180–185
9. Mosqueda-Jimenez DB, Narbaitz RM, Matsuura T, Chowdhury G, Pleizier G, Santerre JP (2004) Influence of processing conditions on the properties of ultrafiltration membranes. J Membr Sci 231:209–224
10. Wienk IM, Boom RM, Beerlage MAM, Bulte AMW, Smolders CA (1996) Recent advances in the formation of phase inversion membranes made from amorphous or semi-crystalline polymers. J Membr Sci 113:361–371
11. Chaturvedi BK, Ghosh AK, Ramachandran V, Trivedi MK, Hanra MS, Misra BM (2001) Preparation, characterization and performance of polyethersulfone ultrafiltration membranes. Desalination 133:31–40
12. Ochoa NA, Pradanos P, Palacio L, Pagliero C, Marchese J, Hernandez A (2001) Pore size distributions based on AFM imaging and retention of multidisperse polymer solutes: characterisation of polyethersulfone UF membranes with dopes containing different PVP. J Membr Sci 187:227–237
13. Han MJ, Nam ST (2002) Thermodynamic and rheological variation in polysulfone solution by PVP and its effect in the preparation of phase inversion membrane. J Membr Sci 202:55–61
14. Idris A, Zain NM, Noordin MY (2007) Synthesis, characterization and performance of asymmetric polyethersulfone (PES) ultrafiltration membranes with polyethylene glycol of different molecular weights as additives. Desalination 207:324–339
15. Deniz S (2006) Characteristics of polycarbonate membranes with polyethylene glycol prepared via dry/wet-phase inversion methods. Desalination 200:42–43
16. Zheng QZ, Wang P, Yang YN (2006) Rheological and thermodynamic variation in polysulfone solution by PEG introduction and its effect on kinetics of membrane formation via phase-inversion process. J Membr Sci 279:230–237
17. Kim IC, Lee KH (2004) Effect of poly(ethylene glycol) 200 on the formation of a polyetherimide asymmetric membrane and its performance in aqueous solvent mixture permeation. J Membr Sci 230:183–188
18. Mansourpanah Y, Madaeni SS, Rahimpour A, Farhadian A, Taheri AH (2009) Formation of appropriate sites on nanofiltration membrane surface for binding TiO_2 photo-catalyst: performance, characterization and fouling-resistant capability. J Membr Sci 330:297–306
19. Smolders CA, Reuverse AJ, Boom RM, Wienk IM (1992) Microstructures in phase-inversion membranes. Part 1. Formation of macrovoids. J Membr Sci 73:259–275
20. Ma Y, Shi F, Ma J, Wu M, Zhang J, Gao C (2011) Effect of PEG additive on the morphology and performance of polysulfone ultrafiltration membranes. Desalination 272:51–58
21. Mohammadi T, Saljoughi E (2009) Effect of production conditions on morphology and permeability of asymmetric cellulose acetate membranes. Desalination 243:1–7
22. Idris A, Yet LK (2006) The effect of different molecular weight PEG additives on cellulose acetate asymmetric dialysis membrane performance. J Membr Sci 280:920–927
23. Chuang WY, Young TH, Chiu WY, Lin CY (2002) The effect of polymeric additives on the structure and permeability of poly(vinyl alcohol) asymmetric membrane. Polymer 41:5633–5641